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Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
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Process for obtaining a synthetic organic fiber or film with high tensile strength

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PROCESS FOR OBTAINING A SYNTHETIC ORGANIC FIBER OR FILM WITH HIGH TENSILE STRENGTH

The invention pertains to a fiber and a process for obtaining a synthetic organic fiber or film with high tensile strength.

For many high-tech applications it is important to use fibers and films with high tensile strength. These so-called high-performance fibers or films may be organic-based (e.g. para-aramid fibers and films or carbon fibers) or inorganic (e.g. E-glass fibers, silicon carbide fibers). They find application in numerous specialty products for automotive, aerospace and ballistic applications, reinforcement of constructions, offshore exploration, protective apparel, sports equipment, and thermal insulation. Each type of high-performance fiber or film excels in certain niche applications.

A special type of high performance fibers is high-modulus high-tenacity fibers. Organic members of this group contain covalent (one-dimensional) chains that are held together by intermolecular interactions. Typical examples are ultra-high-molecular weight poly ethylene (UHMW PE) like Dyneema® and Spectra®, para-aramids like Kevlar®, Technora® and Twaron®, aromatic homocyclic polyesters like Vectran®, and aromatic heterocyclic rods like PBO (Zylon®) and PIPD (M5) based on pyridobisimadazole.

The para-aramids have a well-balanced performance in terms of mechanical properties, chemical resistance and thermal resistance. Consequently, these fibers are used in a variety of application areas, such as optical fiber cables (aerial and duct-in), ballistics (helmets, vests, hard ballistics), composites (engineering plastics, reinforcement of constructions), elastomer reinforcement (tires, hoses, belts), friction/sealing (gaskets, friction, paper, packings), and linear tension members (ropes, cables and thermoplastic pipes). UHMW PE is applied in ropes, cordage, nets, and ballistic protection, but not in applications were creep (e.g. aerial cables) and/or thermal resistance (e.g. automotive hoses) are important. Vectran® is used especially in ropes and cables for offshore exploration, halyards for racing yachts and restraint lines for racing cars, where dynamic loadings require good fiber-to-fiber abrasion resistance and good bend-over-sheave properties. Other applications are protective gloves, sports equipment and insulating paper. PBO combines high modulus and tenacity

with good thermal properties and flexibility, making it suitable in ballistics, flame resistant work wear for fire fighters and heat resistant felts. Application in structural composites, however, is limited by its low compressive strength. The new fiber M5 is a PBO-like fiber with significantly improved compression behavior.

Up to now it is believed that the above fibers span an impressive range in tensile properties, some of them even within one fiber type. Nevertheless, when the tensile strengths could be increased further, a substantial improvement could be obtained, even making available new applications that are not yet possible with the existing high-performance fibers. For PIPD the conventional technique of spinning, air gap drawing, and heat treatment has been described in EP 0,696,297, which technique is considered the closest prior art.

It was now found that a substantial increase of tensile strength, up to a factor 2 or even more, and an increase of the modulus was obtained by using a novel process for obtaining a synthetic organic fiber or film with high tensile strength comprising spinning a synthetic organic polymer to a fiber or extruding the synthetic organic polymer to a film, followed by loading the fiber or film in the presence of a processing aid, at a temperature below the boiling point of the processing aid and above –50°C, at a tension of 10 to 95% of the fiber or film breaking strength, followed by removing the processing aid and/or performing a heating step at a tension of 10 to 95% of the fiber or film breaking strength.

According to the existing methods, the orientation and the modulus of fibers and films is improved by a heat treatment under tension. So, for instance, an oven is used for fibers which consists of a (quartz) tube. Into the tube, slightly above the bottom, a flow of nitrogen is introduced. Its flow rate can be controlled and it can be heated. The nitrogen flow is used to heat the fiber and in addition serves as an inert atmosphere. The fiber is suspended from an upper-clamp, through the oven. To its lower end, a weight is connected which applies the tension during the treatment. Both, oven and upper-clamp are mounted to a solid frame. A specific after-treatment can be carried out as follows. For instance, as-spun PIPD fiber, conditioned at 21°C and a relative humidity of 65%, was clamped into the device as described above. Initially, no tension was applied. Then, the tension was applied and subsequently the fiber was subjected to one, but preferably more treatments at different temperatures. The best results were achieved with a tension of 300 mN/tex and three periods of heating of 30 sec, at 150°C, 350°C, and 550°C, respectively. For the evaluation of the mechanical properties, only the part of the fiber was used that was in the heated area of the oven. The mechanical properties measured are filament properties. They are determined for 50 to 75 filaments by means of a Favimat™ (Textechno, Mönchengladbach, Germany). The average values of the breaking tension and the modulus of the filaments were found to

be 2400 mN/tex and 290 Gpa, respectively, measured on 75 filaments. The original strength and modulus of the filaments was 2100 mN/tex and 170 GPa respectively. For films the measurements were done similarly as is known the skilled person.

According to the method of the present invention the similar after-treatment device is used. However, it was modified in two respects. In the first place a second clamp (the under-clamp) was mounted on the frame, below the first clamp (upper-clamp) and the heating zone. With this under-clamp closed, the length of the piece of fiber in the device is fixed and does not change during the treatment. Further, a facility to cool down the nitrogen flow to temperatures below room temperature is introduced.
A specific after-treatment for fibers is carried out as follows. For instance, a PIPD as-spun fiber, conditioned at 21°C and a relative humidity of 65%, is clamped into the device with the under-clamp open. Initially, no tension is applied. Then subsequently, the fiber is cooled down preferably below room temperature, and more preferably less than 7°C, for instance to 5°C, a tension is applied to the fiber (for instance, about 800 mN/tex) and this tension and temperature are maintained for example for 6 sec. Thereafter, the under-clamp is closed i.e. the strain (elongation) of the fiber is fixed and heat treatment is started. In this particular case the temperature was raised steadily, from 5°C to 500°C in 180 sec.
For the evaluation of the mechanical properties, only the part of the fiber was used that was in the heated area of the oven. The mechanical properties measured are filament properties. They are determined as above using 50 to 75 filaments by means of a Favimat™ (Textechno, Mönchengladbach, Germany). The average values of the breaking tension and the modulus of the filaments were found to be 3600 mN/tex and 320 Gpa, respectively, measured on 75 filaments.

The method of the invention can be used for any synthetic organic fiber or film, but is preferably used for cellulose, rigid rod and aramid fibers and films, more preferably PBO, PIPD, and para-aramid. The linear density of the filaments is preferably 0.1 to 5000, for multifilaments preferably 0.5 to 5, more preferably 0.8 to 2 dtex.

The fibers contain one (monofilament) or at least two filaments (multifilament), specifically 2 to 5000, and more specifically 100 to 2000. Fibers with about 1000 filaments are commonly used.

The processing aid may be any inert liquid, such as water, acid (e.g. phosphoric acid, sulfuric acid), base (e.g. ammonia), aqueous salt solutions (e.g. sodium chloride, sodium sulfate),

and organic compounds (e.g., ethanediol, methanol, ethanol, NMP). The processing aid is preferably an aqueous solution, and with more preference water.

For the method of the invention preferably as-spun fiber, not having received any substantial thermal mechanical after-treatment, is used. When the fiber is produced by wet spinning and water or an aqueous solution is used as the coagulation medium and/or water or an aqueous solution is used for neutralization and washing, the as-spun fiber may contain up to more than 100 wt.% of water and after conditioning at 21°C and a relative humidity of 65%, the as-spun water content may be more than 5 wt.%, typically more than 8 wt.%. In the case of PIPD the as-spun moisture content after conditioning is about 20-24 wt.% (based on dry polymer).

The tension applied during loading is 10 to 95% of the breaking strength of the fiber or film, which is higher than the conventionally used tensions. For instance, in a conventional spinning process of para-aramid fibers based on p-phenyleneterephthalamide the loading before drying does not exceed 5% of the breaking strength of 2000 mN/tex. More preferably, the tension is at least 15% and not more than 80%, most preferably 25 to 60% of the breaking strength of the as-spun fiber.

The temperature upon loading is below the boiling point of the processing aid and at least -50, preferably at least -18°C, and may be near or just above the temperature at which the local thermal transition of the fiber or film starts as determined with DMTA. For PIPD the local transition temperature starts at about -50°C. Typical loading times before heating are 0.1 to 1000 sec. For PPTA (poly p-phenyleneterephthalamide) the transition temperature is also as low as –50°C. Although loading can also be performed at such low temperatures, this is practically less favorable because of the high costs of cooling.

The heating step includes a temperature above the boiling point of the processing aid and may proceed at one temperature or in stages at different temperatures, at atmospheric pressure, at expanded pressure, or, at reduced pressure to promote the removal of the processing aid from the fiber. The heating step is preferably performed at a temperature of 100°C up to 50°C below the melting or decomposition temperature of the fiber, e.g. in the case of para-aramid, PIPD and PBO 120 to 450°C, more preferably 125 to 350°C, and most preferably, 130 to 250°C for a time between 0.1 sec to 1 h, preferably 1 to 300 sec. To prevent breaking of the fiber at high temperatures, it may be necessary to decrease the loading gradually during the heating step.

The invention further pertains to a synthetic organic PIPD fiber with a linear filament density between 0.1 and 500 dtex and a tensile strength higher than 3200 mN/tex.
Preferably the tensile strength is higher than 3300, more preferably higher than 3500 mN/tex.

Favimat measurements

50-75 filaments were randomly selected from a piece of 100 mm of a fiber and suspended in the fiber magazine of a Favimat (Textechno, Mönchengladbach, Germany) with pre-tension weights of 50 mg. From each filament the fineness and its force-elongation curve were determined automatically, using the test conditions:

temperature	21°C
relative humidity	65%
gauge length	25.4 mm
fiber count pre-tension	1.0 cN/tex
clamp speed	2.54 mm/min

As values for the mechanical properties, the average values of the properties of the filaments were taken.

Claims:

1. A process for obtaining a synthetic organic fiber or film with high tensile strength comprising spinning a synthetic organic polymer to a fiber or extruding the synthetic organic polymer to a film, followed by loading the fiber or film in the presence of a processing aid, at a temperature below the boiling point of the processing aid and above –50°C, at a tension of 10 to 95% of the fiber or film breaking strength, followed by removing the processing aid and/or performing a heating step at a tension of 10 to 95% of the fiber or film breaking strength.
2. The process according to claim 1 wherein as-spun fiber is subjected to the loading step.
3. The process according to claim 1 or 2 wherein the loading step is performed between -18 and 20°C, preferably between 0 and 7°C.
4. The process according to any one of claims 1 to 3 wherein the heating step is performed at 100°C or higher.
5. The process according to any one of claims 1 to 4 wherein the processing aid is an aqueous solution, preferably water.
6. The process according to any one of claims 1 to 5 wherein the processing aid is removed simultaneously with performing the heating step.
7. The process according to any one of claims 1 to 6 wherein the synthetic organic fiber or film is a rigid rod or an aramid fiber or film.
8. A synthetic organic fiber, characterized in that the fiber is PIPD with a linear filament density between 0.1 and 500 dtex and a tensile strength higher than 3200 mN/tex.
9. A synthetic organic fiber according to claim 8, characterized in that the tensile strength is higher than 3500 mN/tex.

Abstract

The invention pertains to a process for obtaining a synthetic organic fiber or film with high tensile strength comprising spinning a synthetic organic polymer to a fiber or extruding the synthetic organic polymer to a film, followed by loading the fiber or film in the presence of a processing aid, at a temperature below the boiling point of the processing aid and above -50°C, at a tension of 10 to 95% of the fiber or film breaking strength, followed by removing the processing aid and/or performing a heating step at a tension of 10 to 95% of the fiber or film breaking strength.